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Hazards Associated with Bis(alkynyl)mercurials

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Summary: Caution is advised in the manipulation of bis(alkynyl)mercurials, which, following a spontaneous detonation of $Hg(C\equiv C^iPr)_2$*, should now be considered to be potentially explosive.*

Before the advent of modern spectroscopic methods for compound characterization, the conversion of an organic compound to a crystalline derivative was common practice. In the case of terminal alkynes, bis(alkynyl)mercurials $Hg(C\equiv CR)_2$ were often the derivative of choice.[1] Accordingly, melting points for numerous derivatives have been noted without further comment. Bis(alkynyl)mercurials are in general comparatively high melting crystalline solids that are aerobically and hydrolytically stable. They are trivial to prepare and thereby serve as convenient reagents for transition metal alkynyl chemistry. Reactions of $Hg(C\equiv CR)_2$ with low-valent late transition metal centers may result in insertion of the metal into one Hg−C bond (e.g., $[IrCl(C\equiv CPh)(HgC\equiv CPh)(CO)(PPh_3)_2]$[2]), or in some cases such species may evolve elemental mercury, providing a catalytic process for the synthesis of symmetrical 1,3-diynes.[3] Various simple halide complexes of platinum react cleanly via halide/acetylide transmetalation,[4] while in the case of $[RuCl_2(CO)_2(PMe_2Ph)_2]$ a more complex reaction provides a β-chloromercuriobutenynyl complex.[5] Bis(alkynyl)mercurials react with various group 8 metal hydrido complexes to provide alkynyl[3b,6] or α-(alkynyl)alkenyl[7] complexes or alternatively 1,3-diynes via catalytic demercuration.[4b] Within lanthanide chemistry, bis(alkynyl)mercurials have proven particularly effective in redox transmetalation, providing access to alkynyl derivatives of Ln^{II} and Ln^{III}.[8] In bi- and polynuclear systems they have been shown to provide $C\equiv CR$, $RC\equiv CC\equiv CR$, or $HgC\equiv CR$ fragments.[9] The mercury center displays weak Lewis acidity,[10] such that in reactions with nucleophilic complexes these reagents can effectively serve as electrophilic alkynyl equivalents, following mercury extrusion.[11] Taken together these reactions indicate that bis(alkynyl)mercurials have much to offer as synthetic reagents, including reactivity that is occasionally unique.

We have over the course of 15 years routinely employed bis(alkynyl)mercurials without incident. However, we had reason to prepare a sample of $Hg(C\equiv C^iPr)_2$, an unknown compound that nevertheless was readily obtained via the conventional reaction of $HC\equiv C^iPr$ with basic $K_2[HgI_4]$.[1] A ca. 0.5 g sample of this had been stored in a freezer (−15 °C) and while left *undisturbed* to warm to room temperature spontaneously detonated with considerable force and sound, shattering the glass vial and producing a gray-white cloud (metallic odor) and dispersing finely divided mercury. Thus the explosion hazard is compounded by attendant toxicity and decontamination issues.

We are naturally disinclined to resynthesize this compound to investigate the cause of the explosion; however, we note the following: (i) Bis(alkynyl)mercurials are known to crystallize with mercurophilic interactions that bring adjacent alkynyl groups within close proximity.[12] Thus a phase change upon warming may have generated sufficient pressure to cause explosive demercuration, which given our catalytic studies, is by necessity an exothermic process. (ii) We have observed that samples of $Hg(C\equiv CFc)_2$ (Fc = ferrocenyl) that are not immediately purified by recrystallization (filtration through diatomaceous earth) deteriorate rapidly even when stored in a freezer. Purified samples are however indefinitely stable, leading us to suspect that adventitious elemental mercury (an occasional side product of the synthesis) may facilitate decomposition. (iii) Pure samples of $Hg(C\equiv CPh)_2$ and $Hg(C\equiv C^nBu)_2$ were repeatedly cycled through their melting points without any sign of detonation, suggesting that the behavior might be peculiar to the ^{i}Pr derivative.

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Given the above observations, we would recommend[13] the following: (a) Where possible only small amounts of bis(alkynyl)mercurials should be prepared. (b) Samples should be purified immediately via filtration of their solutions (e.g., $CHCl_3$) through diatomaceous earth.[14] (c) Crystalline samples should neither be heated nor cooled unnecessarily. (d) As always, manipulations should be performed in a well-vented fume cupboard with protective eye-ware, gloves, and ideally an explosion shield.

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(13) These recommendations are given in good faith and do not constitute any liability on the part of the author or journal nor any assurance that adherence will ensure against mishap.

(14) In the usual method for the synthesis of bis(alkynyl)mercurials, an ethanolic solution of the alkyne is added dropwise to an ice-cooled aqueous solution of basic $K_2[HgI_4]$. Elemental mercury (and presumably diyne) can form if the addition is too hasty or if the reaction mixture is allowed to warm above 0 °C.